

**VAPOUR PRESSURE OF ACETONITRILE DETERMINED BY
COMPARATIVE EBULLIOMETRY¹**

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ABSTRACT

The vapour pressures of acetonitrile have been measured over the range (278 K, 4.3 kPa) to (540 K, 4455 kPa). The upper limit exceeds the temperature at which decomposition of acetonitrile begins (about 536 K) so we were able to assess the effect of pyrolysis on the vapour pressures. Acetonitrile is strongly hygroscopic, and a comparison of results obtained with “wet” and “dry” samples allowed us to investigate in a similar way the effect of water as an impurity. The results have been correlated using generalised Wagner equations a key feature of which is the use of the reversed reduced temperature $\tau = 1 - T/T_c$ where T_c is the critical temperature. The standard form with terms in $\tau, \tau^{1.5}, \tau^{2.5}$, and τ^5 produced unacceptable systematic deviations; but the Wagner equation:

$$\ln(p/p_c) = (T_c/T) \left(c_1\tau + c_{1.5}\tau^{1.5} + c_2\tau^2 + c_{2.5}\tau^{2.5} + c_{5.5}\tau^{5.5} \right)$$
, fits our results from 291 K to 535 K with a standard deviation of 63×10^{-6} in $\ln p$ and significantly extends the range of correlation, towards both the triple and critical points, compared with work already in the literature. By extrapolation we obtain 4835 kPa for the critical pressure p_c , and 167 Pa for the triple-point pressure.

KEY WORDS: acetonitrile; boiling point; critical point; ebulliometer; triple point; vapour pressure; Wagner equation.

1. INTRODUCTION

Vapour pressures of pure substances can be measured accurately and rapidly using comparative ebulliometry[1-5]. The sample and a reference fluid are boiled, in separate ebulliometers, under a common pressure of gas such as helium or nitrogen and the condensation temperatures T_s of the sample and T_r of the reference are measured. The common pressure is calculated from the known p, T behaviour of the reference fluid as $p(T_r)$ to give a state point (p, T_s) for the sample. The method has many advantages: direct measurement of pressure is avoided, the fluids are degassed by boiling, and the ebulliometers act as heat pipes to provide high-performance thermostats. The corresponding disadvantages are the considerable demands on thermometry, the solubility of the buffer gas at high pressures, and thermal gradients due to pressure heads although these are readily calculated and are invariably small compared to the gradients in a static apparatus. But the greatest advantage is speed of measurement: typically a (p, T) can be obtained in an hour compared with perhaps a day for a dew pressure in a static experiment.

Acetonitrile is an important organic solvent for polar materials and its vapour pressure has been measured many times although there are large discrepancies among the published values.

2. MEASUREMENTS

The acetonitrile was HPLC grade material supplied by B.D.H. Chemicals with a minimum purity of 99.9 moles per cent and a maximum water content of 0.02 mole per cent. We did not attempt to purify the material by distillation because this would

have had no useful effect on the water content which we anticipated would be the major purity problem. As section 3 shows, water was indeed a serious impurity.

Burfield et al. [6,7] studied the effectiveness of various desiccants and drying regimes for organic solvents. Known amounts of tritiated water were added to rigorously dried solvents and the drying procedures were assessed by the residual water content obtained from the tritium activity. They found that most chemical desiccants were largely ineffective for acetonitrile and only molecular sieves could produce “super dry” acetonitrile with mole fractions of H₂O less than 10⁻⁶. Consequently, we have followed the recommendations of Burfield et al. using 3A molecular sieves, activated at 250 °C, and two-stage drying for periods of 7 d and at least 1 d respectively.

The sample ebulliometer was evacuated for 10 h, with heating to above 100 °C, before loading the acetonitrile while the ebulliometer was flushed with dry argon. A sample (identified as Set A in Table 1) of volume 40 cm³ was used for a series of 25 measurements between (278 K, 4.3 kPa) and (373 K, 175 kPa). A larger 205 cm³ sample (Set B in Table 1) was required at higher reduced temperatures and a second series of 32 measurements were taken covering the range (355 K, 101 kPa) to 535 K, 4175 kPa). The acetonitrile was drawn from the same stock but the samples were dried separately and some contamination with water during transfer to the ebulliometer seems inevitable because acetonitrile is so highly hydroscopic[6,7]. In addition, a set of measurements was made between (354 K, 99 kPa) and (431 K, 703 kPa) with a sample as supplied by B.D.H to investigate the effect of water as an impurity.

The apparatus has been described in detail before [2] and only a brief description is given here. The sample and reference ebulliometers are connected

through metal condensers (cooled with water) and traps (cooled with solid CO₂) to a common pressure line that has a 2 dm³ ballast volume and appropriate gauges and valves that allow the apparatus to be evacuated and pressurised with dry helium. The ebulliometers themselves were constructed from stainless steel tubing and had re-entrant thermometer wells, fitted with twin radiation shields, that provide a depth of immersion for long-stem platinum resistance thermometers of 32 cm in the sample ebulliometer and 45 cm in the reference. We have confirmed experimentally that the temperature difference along the thermometer was attenuated by a factor of 10⁶ for an immersion of only 15 cm[2]. Band heaters (maximum power 140 W) were clamped to the lower 4 cm of the cylindrical boiler and the ebulliometers were thermally insulated very well. However, no secondary heating was used and we relied instead on the exceptionally high thermal conductivity of the ebulliometer, acting as a heat pipe, to eliminate temperature gradients.

Thermometry is especially important in comparative ebulliometry because temperature is the only experimental physical quantity that is required. The thermometers were calibrated on ITS-90 by N.P.L. and their resistance at the temperature of the triple point of water was checked regularly during the project. The pressure was calculated from the condensation temperature on the water using the correlation provided by Wagner [8] for the vapour pressure of water: small corrections were applied for differences in the heads of helium and gaseous water or acetonitrile.

The measurements were always taken with increasing pressure to avoid the possibility of cross contamination between water and sample during depressurisation. Similarly, the apparatus was always left under pressure during a break in the measurements. Up to 4 h were required to obtain the first point when the apparatus

was initially at room temperature but, thereafter, equilibration was obtained within an hour after an increase in pressure.

3. RESULTS AND DISCUSSION

Wagner [9] has developed a family of equations for correlating vapour pressures. The general form of the equation is:

$$\ln(p/p_c) = (T_c/T) \sum_i c_i \tau^i \quad (1)$$

where T_c and p_c are the critical temperature and pressure and

$$\tau = 1 - T/T_c \quad (2)$$

is a reversed reduced temperature variable. The summation provides a bank of terms with integral and half-integral powers of τ from which the form of the correlating equation can be determined. In practice, terms in τ and $\tau^{1.5}$ are always present, and a standard form:

$$\ln(p/p_c) = (T_c/T) (c_1 \tau + c_{1.5} \tau^{1.5} + c_{2.5} \tau^{2.5} + c_5 \tau^5) \quad (3)$$

has proved to be satisfactory for most sets of results. An alternative standard form with terms in τ^3 and τ^6 , rather than $\tau^{2.5}$ and τ^5 , is also widely used. However, additional, and alternative, terms have been required when the data were particularly precise or extensive[2,8-11].

Critical temperatures are readily determined (for example, by direct observation in a sealed tube) but critical pressures are much more challenging and reliable experimental values are rare especially for organic fluids. Equation (1) is readily modified by taking $\ln p$, rather than $\ln(p/p_c)$, as the objective function in the regression analysis and treating $\ln p_c$ as an adjustable parameter. We have demonstrated [1] that Wagner equations are remarkably successful in extrapolating

reliably to the critical pressure from surprisingly low reduced temperatures.

Consequently, our preferred approach now is to combine our vapour pressures with literature critical temperatures to obtain the critical pressure p_c from the regression analysis. For acetonitrile, we have also obtained the triple-point pressure by extrapolation.

Here we use Wagner equations to assess the internal consistency of our two sets of results, separately and combined. Trejo and McLure[12] reviewed the critical properties of acetonitrile and we have adopted their experimental value, which adjusted to ITS-90, is $T_c = (545.46 \pm 0.3) \text{ K}$.

Table 1 lists the vapour pressures of acetonitrile obtained with two sample that were dried separately. The results in Set A cover the range (278 K, 4.3 kPa) to (373 K, 175 kPa) and those in Set B the range (354 K, 101 kPa) to (535 K, 4175 kPa). The first five points of Set A at temperatures $277.9 < T/\text{K} < 288$ are discussed below but were not used for the final regression analyses.

The 29 results of set B for the larger sample were correlated by the equation

$$\ln p = \ln p_c + (T_c/T) \left(c_1 \tau + c_{1.5} \tau^{1.5} + c_2 \tau^2 + c_3 \tau^3 \right) \quad (4)$$

where $T_c = 545.46 \text{ K}$, $p_c = 4836.3 \text{ kPa}$, $c_1 = -7.601380$, $c_{1.5} = 0.074994$, $c_2 = 2.323761$, and $c_3 = -3.640424$; with standard deviations σ of 13×10^{-6} in $\ln p$ and 0.7 mK in the condensation temperature T . By contrast, the standard form of the Wagner equation (3) gave a comparatively poor fit to the same data with standard deviations $\sigma(\ln p) = 141 \times 10^{-6}$ and $\sigma(T) = 8.1 \text{ mK}$ with large systematic deviations. Such a comparison illustrates the difficulties of correlating vapour pressures and suggests that our results happen to be well conditioned to the form (4). Nevertheless, such a high level of internal consistency for the results is most pleasing considering

that our estimated precision in the condensation temperatures of acetonitrile and water was 1 mK.

Three further measurements, not listed in Table 1, were made with this sample at higher temperatures, but these results are clearly affected by decomposition. If the first of these points is included in the regression, then the critical pressure so obtained increase by 1.6 kPa and standard deviations deteriorate significantly:

$\sigma(\ln p) = 54 \times 10^{-6}$, $\sigma(T) = 3.7$ mK. By contrast, if the final point (535.032 K, 4174.613 kPa) listed in Table 1 is omitted, then there is no change to the standard deviations and the calculated critical pressure increases by only 0.2 kPa. These results suggest that the thermal decomposition begins at a temperature between 535.0 and 536.8 K, which is somewhat higher than the 523 K chosen by Kratzke and Müller[13] as the greatest temperature at which they could work and avoid decomposition.

Figure 1 shows the deviations from equation (4) of the results obtained with sample B, and the abrupt onset of decomposition is clear. Deviations of these data from the standard Wagner equation (3) are also plotted to show the systematic sinusoidal deviations.

The results obtained at lower pressures with sample A are not of such high quality as those in Set B but nevertheless a Wagner equation with terms in $\ln p_c$, τ , $\tau^{3/2}$, and τ^2 fits the data of Set A at temperatures above 290 K with standard deviations of $\sigma(\ln p) = 49 \times 10^{-6}$ and $\sigma(T) = 1.2$ mK. No further terms were significant in the regression, but this equation has one fewer term in τ than is usual for a Wagner equation and the value of the critical pressure obtained was ridiculously high. An Antoine equation is much more convenient for routine calculations at low pressures and

$$\ln(p/\text{kPa}) = 14.7340 - 3268.53/(T/\text{K} - 31.615) \quad (5)$$

fits the results for Set A over the temperature range 290 K to 362 K (or 8 kPa to 125 kPa in pressure) with standard deviations of $\sigma(\ln p) = 61 \times 10^{-6}$ and $\sigma(T) = 1.5$ mK. Figure 2 plots the deviations from the Antoine equation (5) of the results from sample A and those from sample B in the overlapping temperature range. It was difficult to achieve smooth boiling of the water for the five results at very low pressures (4.3 to 7.2 kPa) because the ebulliometers, originally designed for high pressures, were not fitted with bubble caps. These five data have not been included in any of the regression analyses because they fell short of the quality of the other results, but they are plotted in Figure 2 to 5 to show that the deviations from the smoothing equations are very small compared with those for the literature data.

Although the results obtained with samples A and B individually are internally consistent at a very high level and span only 3.7 mK at the normal boiling temperature, it has been rather difficult to combine the two data sets in a way that does justice to their individual merits. Nevertheless, the Wagner equation:

$$\ln p = \ln p_c + (T_c/T) \left(c_1 \tau + c_{1.5} \tau^{1.5} + c_2 \tau^2 + c_{2.5} \tau^{2.5} + c_{5.5} \tau^{5.5} \right) \quad (6)$$

with $T_c = 545.46$ K, which has five terms in τ , fits the combined data sets with standard deviations $\sigma(\ln p) = 63 \times 10^{-6}$ and $\sigma(T) = 2.0$ mK. The regression coefficients in equation (6) were $p_c = 4835.3$ kPa, $c_1 = -7.542771$, $c_{1.5} = -0.549679$, $c_2 = 4.958924$, $c_{2.5} = -5.030732$, and $c_{5.5} = -1.699257$. At low temperatures there are systematic sinusoidal deviations, with extremes of about 3.5 mK, but above 425 K, or 600 kPa in pressure, equation (6) gives an excellent representation of the data and extrapolates smoothly to a critical pressure of (4835 ± 0.7) kPa. The quoted uncertainty in p_c is the standard deviation from the regression to equation (6) but if account is taken of the uncertainty of ± 0.3 K given by Rodriguez and McLure for their measurement of T_c then the error in p_c increases to ± 18 kPa. The agreement

between our calculated value of p_c and Trejo and McLure's direct observation of $(4.83 \pm 0.02)\text{MPa}$ is excellent. The deviations of the experimental condensation temperatures from equation (6) are shown in Figure 3. Although the sinusoidal deviations indicate that the equation is not ideal, the close agreement in the overlapping region between the results obtained with the two samples is very pleasing and, indeed, a standard deviation of 2.0 mK and a maximum deviation of 4 mK over such a wide temperature range is excellent compared with the literature which is discussed below. We also made measurements with a sample that was not dried over molecular sieves to assess the possible affect of water as an impurity. As Figure 3 shows the condensation temperature is elevated by about 16 mK near atmospheric pressure but this is reduced to -3 mK at a pressure of 700 kPa.

Figure 4 compares results from the literature with equation (6) as deviations in $\ln p$. The 14 vapour pressures reported by Kratze and Müller[13] in the temperature 353 to 475 K are in good agreement with our work and have an rms deviation of 0.024 per cent from equation (6), which is significantly less than their estimated accuracy of 0.1 per cent. Other results [14, 15] at high pressure lie 2 or 3 per cent below our measurements. The work of Warowny[22] also lies below us (except for one pressure) but the deviation is only 0.7 per cent on average.

Fractional deviations $\delta \ln p = \delta p / p$ are rather severe at low pressures, so Figure 5 gives the deviations in terms of pressure. Putnam et al.[16] are consistently above our measurements but the average deviation is only 19 Pa; while the work of Meyer et al.[18] is consistently low by up to 96 Pa. The vapour pressure obtained by Dojcansky et al.[17], and by Hall et al.[19] are all significantly below those obtained from equation (6) by up to 1.5 kPa, while the work of Heim et al.[20] cuts across our results with an rms deviation of 60 Pa. Our five results below 8 kPa which we

removed from the regression because the experimental condensation temperatures were unstable are also included in Figure 5: the deviation Δp are in the range 0.9 to 2.5 Pa which, when compared to the literature data, indicates the exacting criteria we have applied to our measurements.

Several correlations have been proposed for the vapour pressures of acetonitrile. The Antoine equation, up to the normal boiling temperature, obtained by TRC and recommended recently by Landolt-Börnstein [21] is based on the work of Putnam[16] and Meyer[18] as Figures 4 and 5 show. However, they also recommend an Antoine equation between the normal boiling temperature and 530 K which is less successful. It gives pressure 700 Pa higher than the low-pressure version at the normal boiling temperature but thereafter the calculated pressures are progressively too low reaching -3.9 per cent at 530 K. Although these deviations are less than the equation's estimated reliability of 5 per cent, an Antoine equation is not really appropriate[33] for fitting vapour pressures above a reduced temperature of about 0.75. The correlations proposed by Yawns[23] and by DIPPR[24] give very similar pressures which is not surprising since they use the same form of equation and have some identical parameters. These two equations relied on Kratze and Müller[13] above atmospheric pressures but, as Figure 4, shows do not reproduce their measurements particularly well.

Extrapolation downwards is a severe test of a vapour pressure equation and Wagner equations are, perhaps, especially susceptible because the reversed temperature variable τ increases at lower temperatures. Frenkel et al.[34] have investigated extrapolation with the standard forms of the Wagner equation and showed that negative values of dp/dT , which leads to negative enthalpies of vaporization, may occur. Putnam et al.[16] report a triple point at $T^{s+l+g} = 229.349$ K

but not the corresponding pressure. DIPPR[24] use the T^{s+l+g} Putnam et al. and a triple-point pressure of $p^{s+l+g} = 187$ Pa. Using equation (6) we obtain (229.349 K, 167 Pa) for the triple point: dp/dT decreases smoothly and is positive at all stages of the extrapolation over 60 K. Consequently, although combination of results obtained with two sample that evidently differed somewhat in their water content lead to a difference of 3.7 mK at the normal boiling temperature and to small systematic deviations from equation (6), such imperfections are very slight compared with the scatter of the data in the literature and the difference of 16 mK that we observed with a sample that had not been dried. We conclude that equation (6) is by far the most reliable equation for the vapour pressure of acetonitrile. In particular, it extrapolates smoothly to both the triple point and the critical point, and the calculated vapour pressures at the extremes of the liquid regime are in excellent agreement with the best estimates in the literature.

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Table 1. Vapour pressures p of acetonitrile at temperature T with deviations $\Delta \ln p$ from the Wagner equation (6).

T/K	p/kPa	$10^2 \Delta \ln p$	T/K	p/kPa	$10^2 \Delta \ln p$	T/K	p/kPa	$10^2 \Delta \ln p$
Set A (not in regression)			345.575	75.440	0.0067	437.302	804.861	0.0015
277.922	4.323	0.0214	349.328	85.311	0.0039	443.496	910.819	-0.0001
278.625	4.490	0.0346	352.879	95.589	0.0047	449.596	1025.474	-0.0021
281.567	5.247	0.0382	354.665	101.120	0.0025	455.736	1151.968	-0.0004
285.376	6.385	0.0361	357.556	110.614	-0.0028	461.874	1290.201	-0.0024
287.667	7.165	0.0350	361.612	125.129	-0.0083	468.370	1450.280	-0.0016
Set A (in regression)			368.966	155.329	-0.0071	474.052	1602.627	-0.0021
290.647	8.296	0.0032	373.17	175.036	-0.0098	479.154	1749.838	-0.0019
292.746	9.182	0.0058	Set B			484.769	1923.878	-0.0019
295.784	10.604	0.0073	354.55	100.745	-0.0085	490.370	2110.770	-0.0006
300.824	13.366	-0.0114	360.942	122.631	-0.0079	495.752	2303.512	-0.0009
303.811	15.271	-0.0118	371.739	168.122	-0.0057	501.480	2523.662	-0.0007
309.636	19.639	-0.0150	378.815	204.592	-0.0037	506.921	2747.952	0.0007
315.433	24.972	-0.0023	384.111	235.792	0.0007	512.610	2999.224	0.0046
321.118	31.311	0.0073	394.294	306.279	0.0038	518.008	3254.077	0.0011
325.022	36.387	0.0117	405.236	399.500	0.0056	523.151	3512.890	0.0007
331.275	45.907	0.0109	415.213	502.665	0.009	527.790	3760.372	0.0012
336.413	55.169	0.0054	423.683	605.601	0.0043	532.079	4001.463	-0.0007
341.179	65.072	0.0064	431.124	708.993	0.0029	535.032	4174.613	-0.0022

Figure Captions

Fig. 1. Deviations ΔT of condensation temperatures of acetonitrile from Wagner

equations with four terms in τ . ●, deviations of Set B from equation (4); ○,

deviations of decomposing sample from equation (4); , deviations of Set B

from standard form (3).

Fig. 2. Deviations ΔT of condensation temperatures of acetonitrile from the Antoine

equation (5). ● Set A for $T > 290.5$ K; ○, Set A for $T < 290.5$ K; , Set B

Fig. 3. Deviations ΔT of condensation temperatures of acetonitrile from the final

equation (6). ■, Set A for $T > 290.5$ K ; ●, Set B; ○, Set A for $T < 290.5$ K; ,

“wet” sample.

Fig. 4. Fractional deviations $\Delta \ln p = \Delta p/p$ of the vapour pressure of acetonitrile from

equation (6). ●, this work included in the regression; ○, this work excluded

from the regression; ■, reference 17; , reference 20; ▲, reference 13; ▼,

reference, 25; |, reference 15; ▽, reference 22; ♦, reference 18; ◇, reference 19;

+, reference 16; −, reference 32; ×, references 27-31; Δ, (critical point) reference

12.

Fig. 5. Deviations Δp of the vapour pressure of acetonitrile from equation (6). ●, this work included in the regression; ○, this work excluded from the regression; ■, reference 17; □, reference 20; ▲, reference 26; ▼, reference, 25; ◆, reference 18; +, reference 16; −, reference 32; ×, references 27-31.

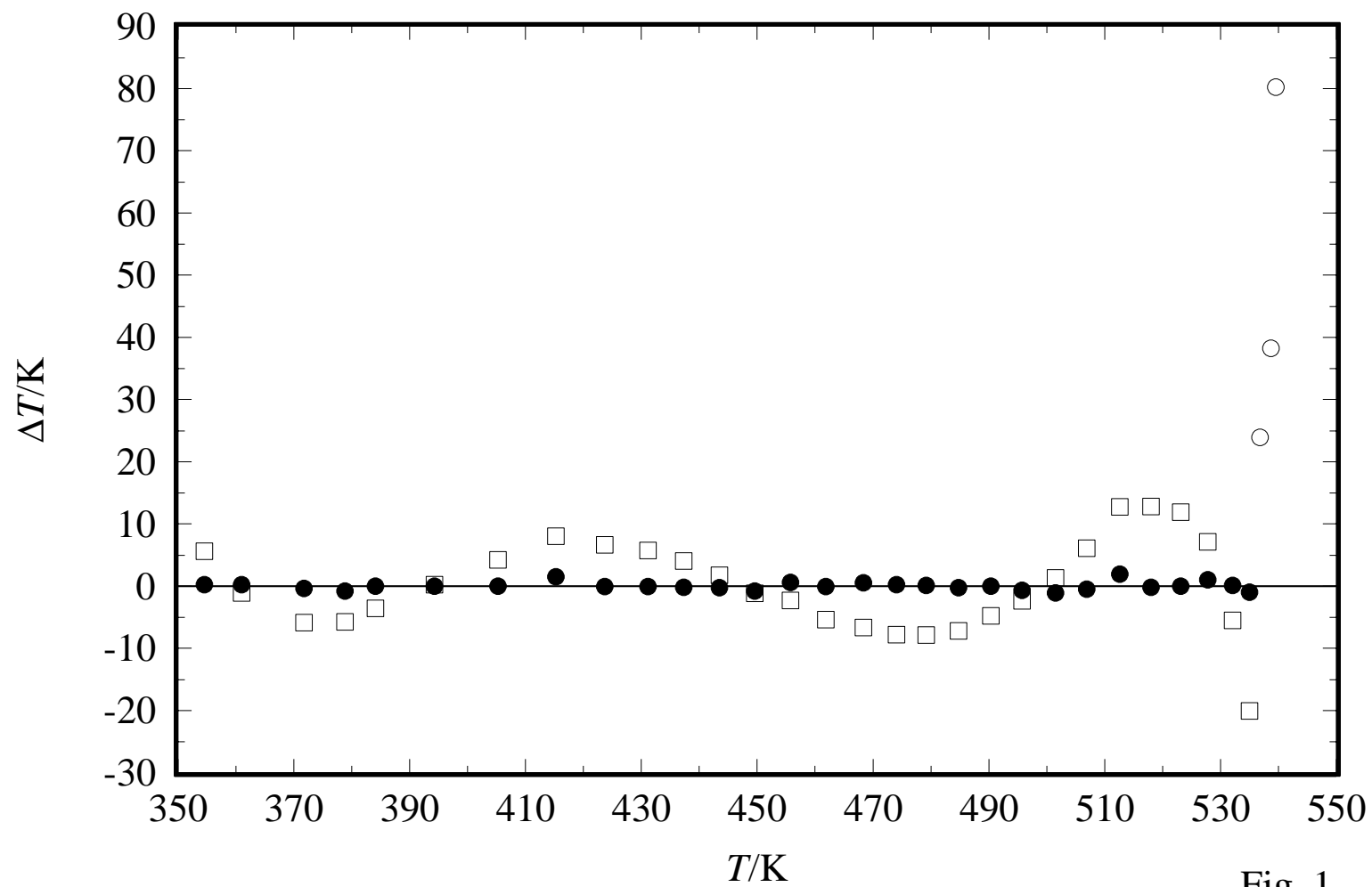


Fig. 1

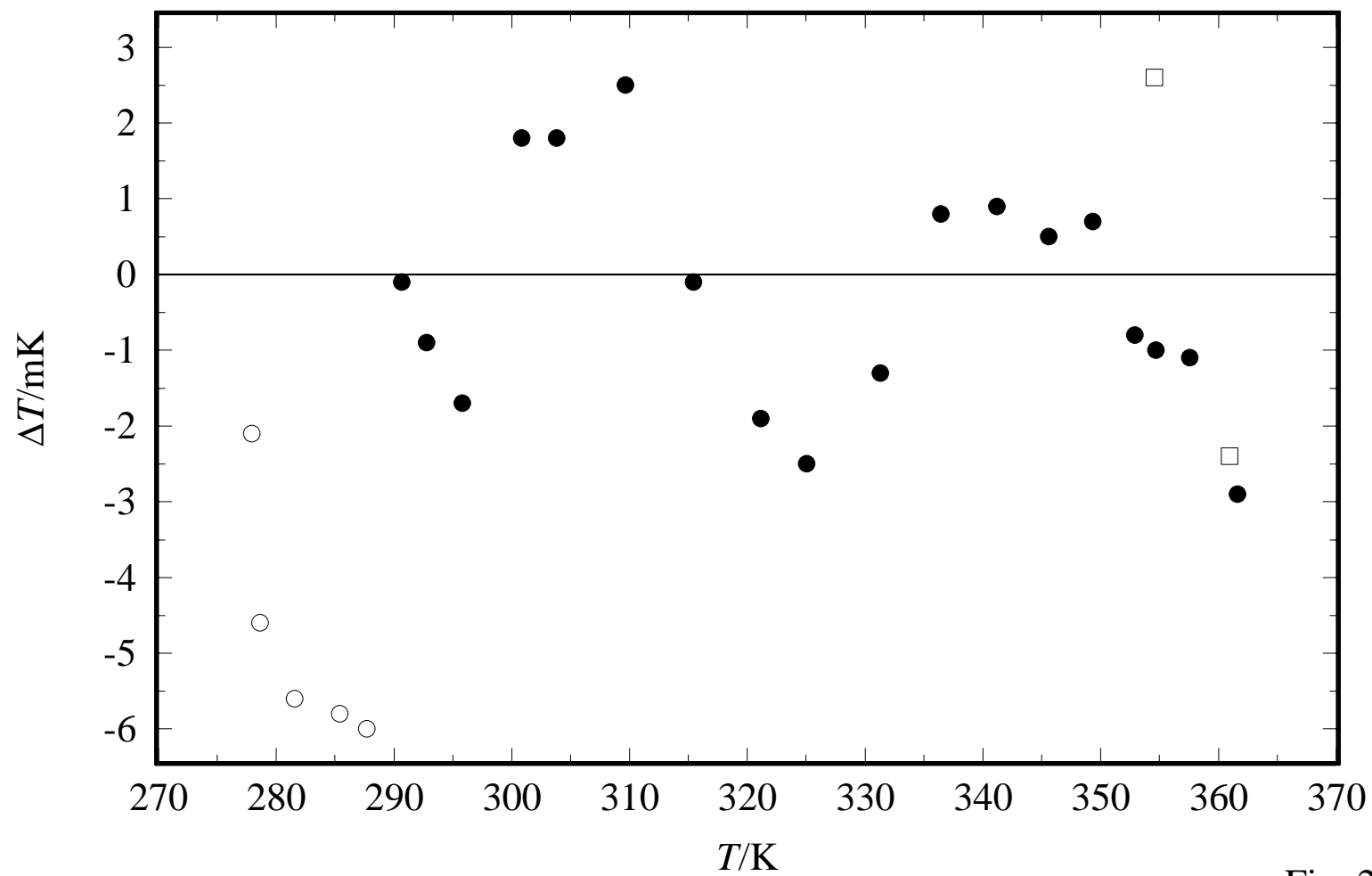


Fig. 2

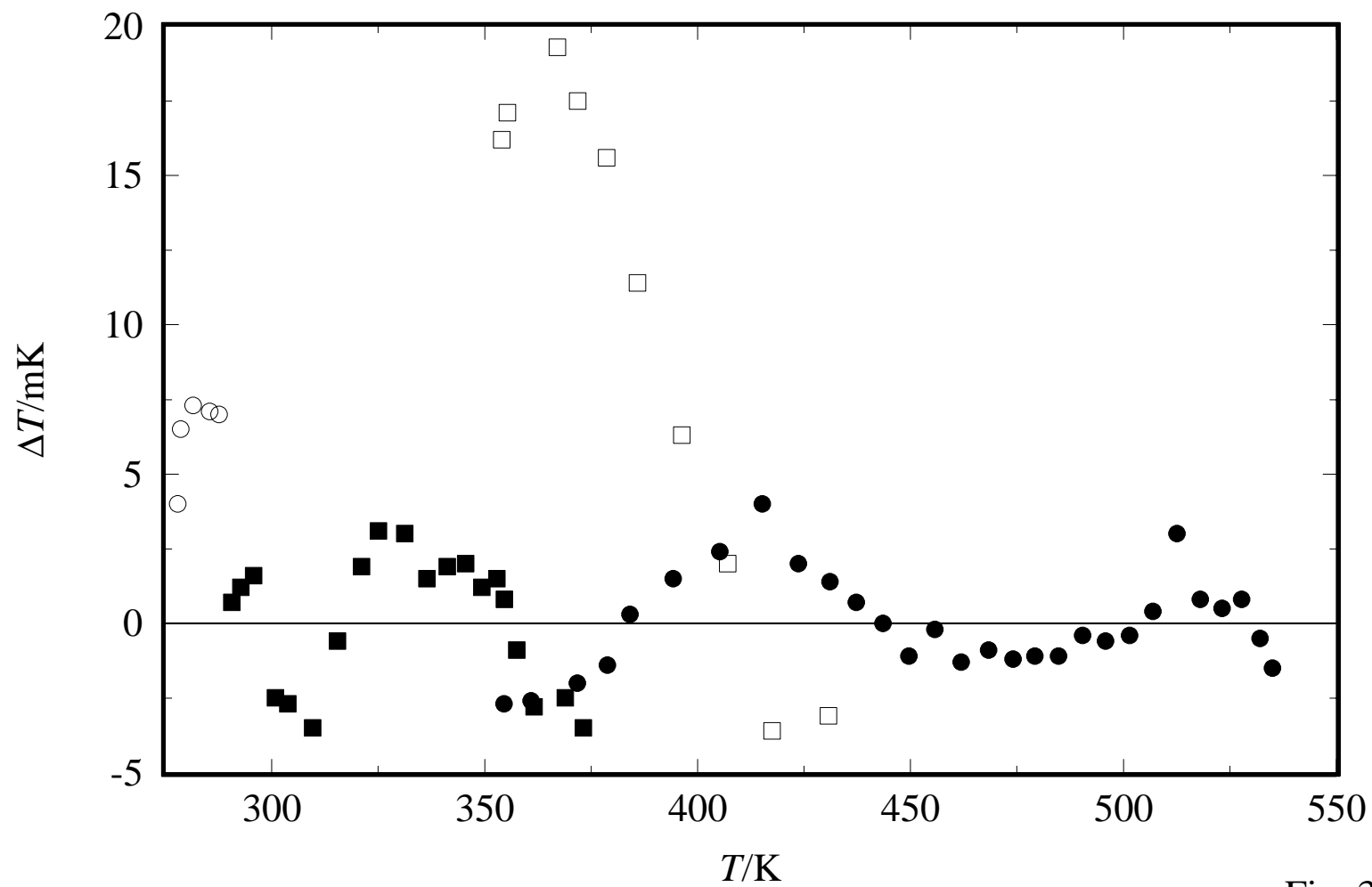


Fig. 3

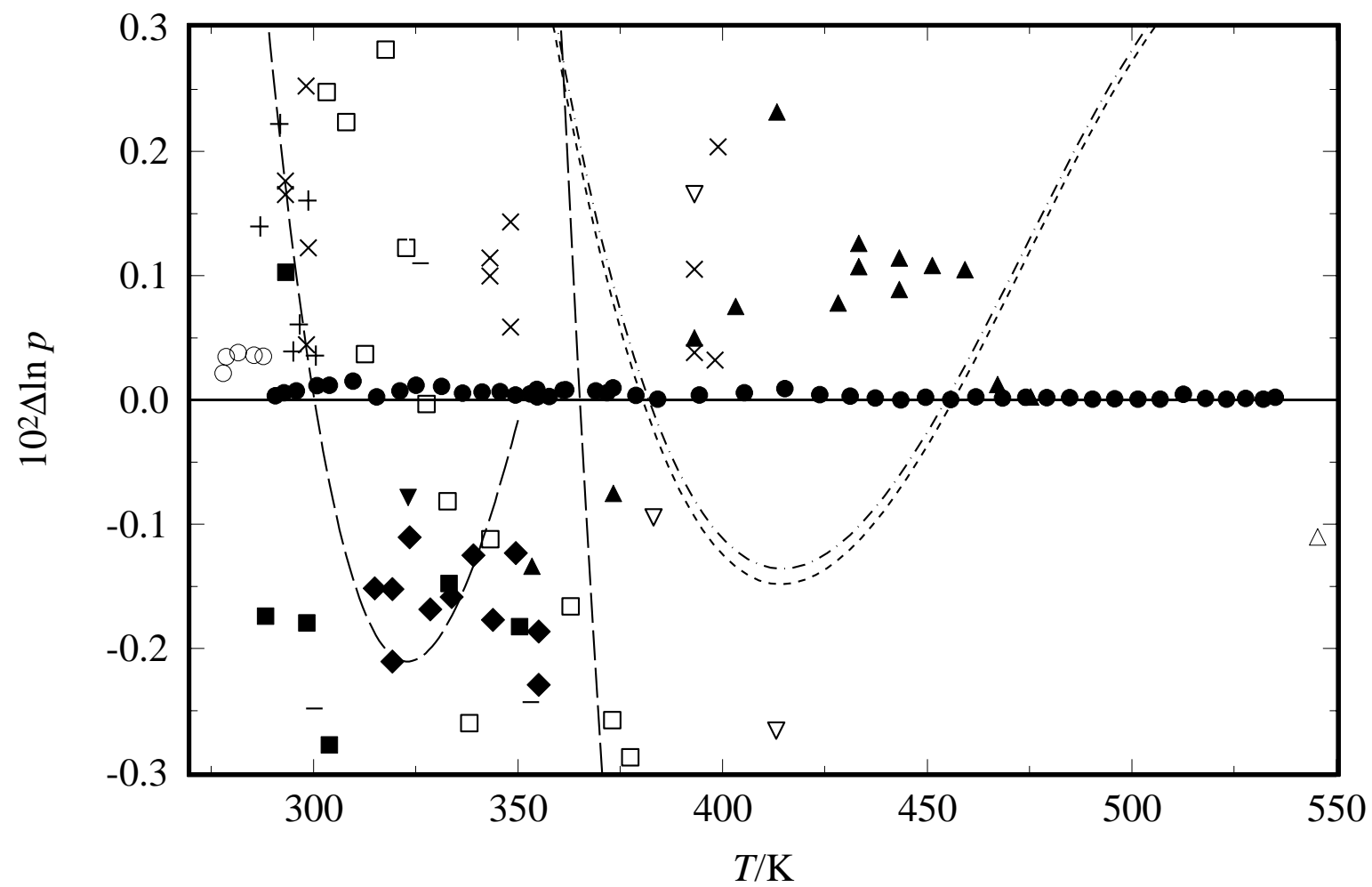


Fig. 4

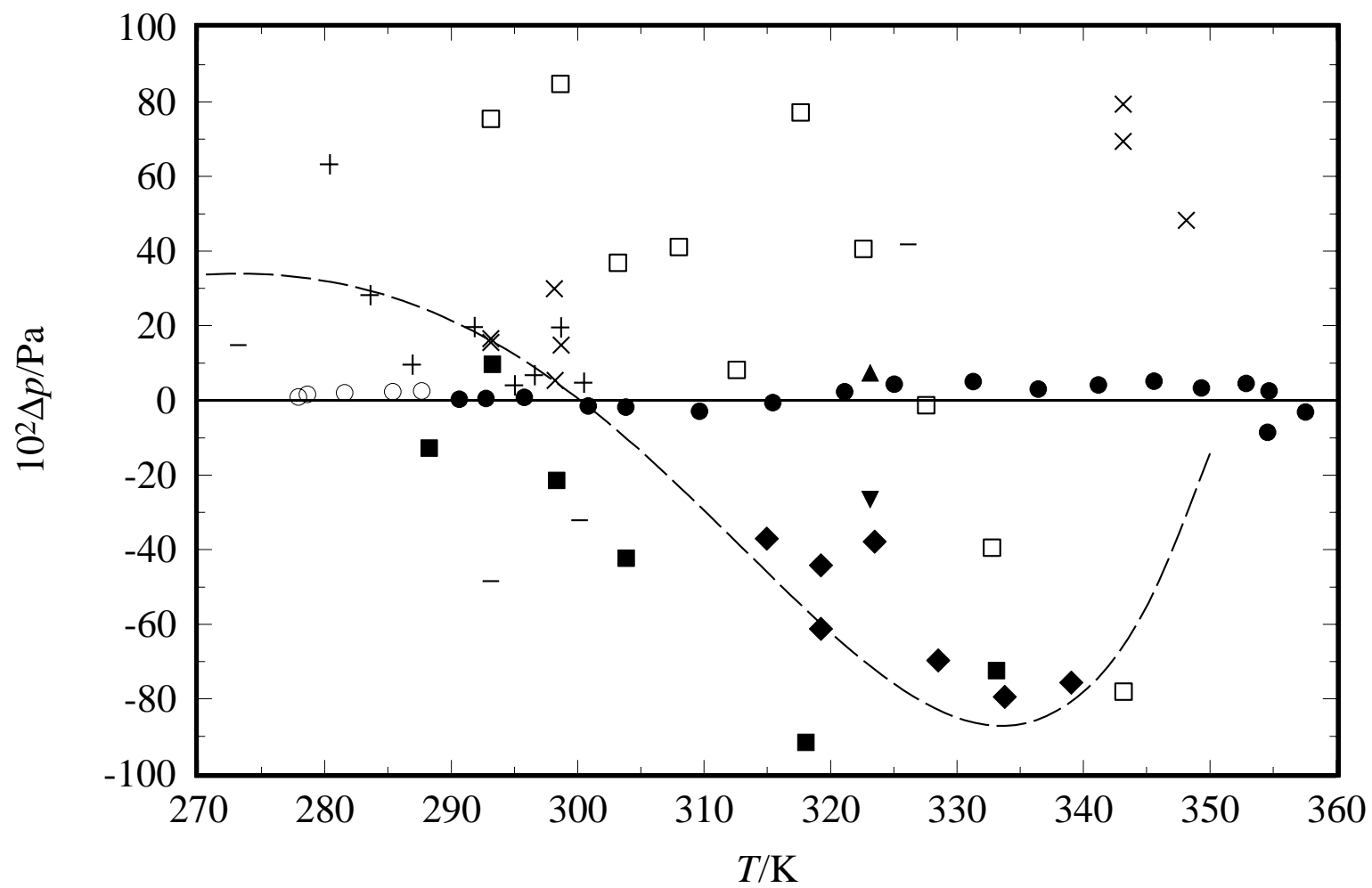


Fig. 5